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THE PRODUCTION OF ITACONIC ACID FROM THE CRUDE ACONITATE OBTAINED FROM SUGARCANE MOLASSES

Pilot-Plant Studies Conducted January to June, 1946

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INTRODUCTION

It has been known since 1873 (1) that esters of itaconic acid may be polymerized to form colorless plastics. These were later shown to have high indexes of refraction (2) and other characteristics which would make them valuable for the production of safety glass and molded resinous products (3). Commercial production of these plastics has not been possible because the best method of making itaconic acid has been by the destructive distillation of citric acid (4). This has not proved to be a practical method for large-scale production due to the very high temperatures required, resulting in such extensive secondary reactions of decomposition, polymerization, and isomerization that the yields of itaconic acid are poor and uncertain. The pyrolytic decomposition of aconitic acid to itaconic acid, first noted in 1840 (5), has had no industrial application because aconitic acid, until recently, has entered commerce in only small amounts as an expensive dehydration product of citric acid (6). Recently the experimental production of itaconic acid by fermentation of carbohydrates has been announced (7).

Aconitic acid was first noted in sugarcane products in 1877 by Behr (8). Aside from the amino acids, it has been shown to be the principal organic acid of cane juice by Yoder (9), by McCalep and Seibert (10), and by Balch, Broeg and Ambler (11). During the processes of sugar manufacture, salts of aconitic acid, i.e., the aconitates, remain in solution when the sugar is crystallized and accumulate in the molasses. In 1944 and 1945 it was demonstrated at the Iberia Sugar Cooperative, Inc., New Iberia, La., that alkaline-earth aconitates may be recovered in commercial quantities from second or "B" molasses (12), and that the molasses from which they have been removed may be used in the sugarhouse without altering any of the processes usually employed for the recovery of sugar. Indications are that each year at least 4,000,000 lbs. of aconitic acid are potentially recoverable in this way as a byproduct from the sugarcane grown and milled in Louisiana and Florida. At present no estimate of the additional amounts of aconitic acid recoverable from imported raw sugars and molasses is possible.

It was noted early in the studies conducted by the Agricultural Chemical Research Division on aconitic acid in sugarcane products that when dilute aqueous solutions of the acid are heated, the aconitic acid is slowly decomposed into itaconic acid and carbon dioxide (11). Further study of this reaction has led to the development of a process for the production of itaconic acid of high purity and in high yield from the crude alkaline-earth aconitate separated from molasses. In this process the preliminary isolation of aconitic acid as such is not necessary and the secondary decomposition, polymerization and isomerization of the pyrolytic processes take place to but a slight extent. The utilization of the aconitate from molasses in this way could lead to the yearly production of at least 2,500,000 to 3,000,000 lbs. of itaconic acid. This report covers the laboratory and preliminary small pilot-plant production of itaconic acid from crude aconitate separated from about 1000 gallons of B molasses obtained from the largest sugarcane mill in Louisiana during the 1945-46 season of operations.

THE CHEMISTRY OF THE PROCESS

Laboratory Studies on the Decarboxylation of Aconitic Acid and Aconitates.

When dilute aqueous solutions of aconitic acid are heated, the acid undergoes decarboxylation, with the formation of carbon dioxide and itaconic acid (11) according to the equation $C_3H_3(COOH)_3 \dashrightarrow CO_2 + C_3H_4(COOH)_2$. The reaction is irreversible since it can be carried out in closed systems under the pressure generated by the carbon dioxide evolved in the reaction as well as at atmospheric or reduced pressures where the carbon dioxide is removed as fast as it is formed. The rate of decarboxylation increases with increase of temperature but decreases with increase of concentration of aconitic acid. When the pH of the solution is changed by adding alkali, it was found that, under reflux at the boiling point, the rate of the reaction is accelerated with the first increments of alkali, increasing to a maximum at pH 2.8 to 3.5, corresponding to the neutralization of 1/6 to 1/3 of the acid, respectively. With more complete neutralization to pH values greater than 3.5, the rate decreases as the pH increases, and when the solutions are made neutral or alkaline no decarboxylation at all takes place. When acids are added to the aconitic acid solutions, the rate is decreased but the reaction is not completely stopped except when the water content of the resulting solution amounts to but a few per cent, as in concentrated sulfuric acid or in glacial acetic acid. At the optimum pH the effect of concentration of the aconitic acid on the reaction rate is practically nullified, so that temperature and pH become the critical variables. See Table I, which gives data bearing on the points discussed.

Theoretically the course of the reaction $C_3H_3(COOH)_3 \dashrightarrow CO_2 + C_3H_4(COOH)_2$

may be followed by titrating the acidity before and after the decarboxylation, or by determining the amount of carbon dioxide produced. Because of secondary reactions, however, the values obtained by titration always indicated a greater decomposition of aconitic acid than those obtained from the carbon dioxide. The simpler technic of the titration led us to use it in the preliminary laboratory experiments, since these values, although too high, corresponded in order of magnitude to the true values for the decarboxylation as determined from the carbon dioxide evolved.

Table I

DECOMPOSITION OF ACONITIC ACID IN AQUEOUS SOLUTION
AS DETERMINED BY LOSS OF ACIDITY

(Values have a large positive error, as explained in the text.)

Concentration of Aconitic Acid	Fraction Neutralized	pH	Time of Heating	Decomposition at Boiling (reflux)	110°	120°	130°	140°
g/100 ml			Hours	%	%	%	%	%
0.05	0	-	2	10.3	-	-	-	-
0.2	0	-	"	8.1	-	-	-	-
1.0	0	2.1	"	3.2	16.4	49.2	93.5	103.2
"	1/6	2.8	"	10.5	49.5	92.4	104.5	105.0
"	1/3	3.5	"	14.6	-	-	-	-
"	1/2	4.2	"	7.8	-	-	-	-
"	2/3	4.9	"	1.8	-	-	-	-
"	all	7.0	"	0.0	-	-	-	-
10.0	0	-	"	2.4	9.5	28.2	69.8	103.8
"	1/6	-	"	49.5	59.0	107.0	110.5	114.0
0.05	0	-	6	26.2	-	-	-	-
"	1/6	-	"	34.8	-	-	-	-
0.2	0	-	"	21.0	-	-	-	-
"	1/6	-	"	35.1	-	-	-	-
1.0	0	-	"	10.7	-	-	-	-
"	1/6	-	"	30.5	-	-	-	-
4.0	0	-	"	6.9	-	-	-	-

Secondary Reactions.

When the decarboxylation was carried out with solutions of pure aconitic acid boiling under reflux, there was a slight secondary reaction which produced a small amount of a yellowish, water-soluble, amorphous material, but there was no detectable amount of citraconic acid formed by isomerization. When the solutions were heated in the autoclave to temperatures above 100° C, the amount of the yellow material was increased somewhat, but still no citraconic acid could be found. However, the decarboxylation of the partly neutralized solution, both by refluxing and by autoclaving, was accompanied by the formation of a few per cent of citraconic acid, except when the neutralizing substances were basic compounds of calcium or barium. That the citraconic acid was formed by the isomerization of the itaconic acid first formed and not by a different mode of decarboxylation of the aconitic acid was demonstrated by boiling partly neutralized solutions of itaconic acid, when it was found that sodium ions induced extensive isomerization, but that calcium ions did not cause production of citraconic acid to any appreciable extent. See Table II.

Since citraconic acid is volatile with steam (13) while itaconic acid is not, the determination of the amount of citraconic acid formed by heating solutions of aconitic acid or itaconic acid was made by acidifying the solutions, subjecting them to steam distillation and titrating the acid in the distillate. Distillation was continued until no more acid for found in the distillate.

Table II

ISOMERIZATION OF ITACONIC ACID TO CITRACONIC ACID

Itaconic Acid	Base Used	Fraction Neutralized	H_2O	Temperature	Time	Citraconic Acid Formed
Grams			ml.	°C	Hours	%
5	-	0	50	Boil, reflux	8	0.39
5	Na_2CO_3	1/4	"	" "	"	1.92
5	-	0	7.5	140	2	1.75
5	Na_2CO_3	1/8	"	"	"	23.34
5	"	1/4	"	"	"	32.80
5	"	1/2	"	"	"	8.71
1.3	-	0	10	"	"	0.0
1.3	Na_2CO_3	1/4	"	"	"	5.0
1	$CaCO_3$	1/3	"	"	"	0.0
1	"	1/4	"	"	"	0.0

Decarboxylation of Calcium-Magnesium Aconitate.

With these facts established, attention was turned to experiments using acidified solutions of aconitates instead of neutralized solutions of the pure acid itself. It was found that at the optimum pH the decarboxylation reaction proceeded in the same way whether the solutions were prepared by neutralizing the acid with bases or by acidifying solutions or suspensions of the aconitates of the corresponding bases. For example, when a suspension of insoluble calcium aconitate in water was acidified with 5/6 the amount of sulfuric acid necessary to combine with the calcium of the aconitate, the decarboxylation proceeded in the same way as when a solution of identical aconitic acid content had been 1/6 neutralized with lime. The precipitated calcium sulfate in such a suspension need not be removed by filtration but may be left in suspension during the decarboxylation. These experiments indicated that the crude calcium-magnesium aconitate obtained from molasses (14), after having been washed free of sugar, could be used directly for the production of itaconic acid without the necessity of first liberating and crystallizing aconitic acid. This was confirmed by experiments in the laboratory autoclave.

Decarboxylations carried out under reflux at the boiling point and at the optimum pH were not complete in 24 hours. In the experiments using the autoclave it was impossible to determine exactly the time for the completion of the reaction, but at optimum pH and 140° C. it was somewhat less than 2 hours. The time required is dependent on the pH of the charge and the temperature of heating, but the exact relationships could not be defined accurately with the equipment at our disposal either in the laboratory or later in the pilot-plant.

PREPARATION OF THE ACONITATE FROM MOLASSES

To obtain the aconitate necessary for pilot-plant studies of its conversion to itaconic acid, Godchaux Sugars, Inc. placed at our disposal a supply of B molasses, 80 Brix solids, produced at its Raceland, Louisiana, mill. This molasses was brought to the Southern Regional Research Laboratory in New Orleans at the close of the 1945 sugar milling season, where it was worked up in the pilot-plant after the Raceland mill had closed.

Characteristics of the Molasses and Laboratory Tests.

This molasses contained 3.5 to 3.8% aconitic acid, based on Brix solids. However, contrary to experience with molasses from some other mills, no aconitate could be separated from it by merely heating the diluted molasses, nor by adjusting the pH with lime to 6.5 to 6.8 and then heating. Analysis of the molasses revealed that it was low in calcium and magnesium, containing but 0.56% and 0.20%, respectively, based on Brix solids. When the percentages of calcium, magnesium and aconitic acid are calculated as molecular ratios (% ÷ atomic or molecular weight x 100), it is found that the sum of the ratios for calcium and for magnesium is to the ratio for aconitic acid as (1.4 + 0.8) : 2.0. Since the insoluble calcium-magnesium aconitate desired (14) has molecular ratios of (calcium + magnesium) : aconitic acid = 3 : 2, it was evident that the molasses did not contain sufficient calcium and magnesium to form the insoluble compound.

Further, a portion of the calcium and magnesium present in the molasses was not available for aconitate formation. When the molasses was diluted and heated, whether or not lime or calcium chloride was added, there separated large quantities of a slimy, amorphous, highly hydrated precipitate. This material clogged the pores of filter paper or cloth almost instantly. It could be removed by centrifuging at high speeds, and when resuspended in water and again centrifuged, it was but incompletely soluble in either strong hydrochloric acid or alkali. It could be dried to a hard mass which did not rehydrate to the original slimy condition, and then it could be easily filtered. This washed and dried material contained 11.2% of calcium and 0.8% of magnesium. Thus there was competition between the aconitate and the amorphous material for the already insufficient quantity of calcium and magnesium in the molasses, and, since the amorphous material was the more insoluble and separated first and the more easily, its precipitation further reduced the amounts of these bases dissolved in the molasses. Obviously the aconitate could be separated only after sufficient soluble calcium had been added to satisfy the requirements of both the amorphous matter and the aconitic acid.

Laboratory tests in which the diluted molasses was limed, treated with calcium chloride and heated, showed that a crystalline precipitate was formed in the hot molasses, but that on cooling these crystals redissolved in the molasses before they could be separated from it. When, however, magnesium chloride was also added, the aconitate separated in beautifully crystalline form and remained insoluble in the molasses as it cooled.

Pilot-plant Studies on Aconitate Recovery.

With the above facts established in the laboratory, the experiments were transferred to the pilot-plant to ascertain the best procedure for recovering the aconitate without impairing the quality of the molasses for further use in sugar manufacture. In these pilot-plant studies attention centered on the effects on the precipitation of the aconitate by variations of (1) molasses concentration (Brix), (2) pH adjustment, (3) the quantities of calcium and magnesium chlorides added, (4) the temperature to which the molasses was heated, (5) the length of time it was heated, and (6) the removal of the aconitate from the molasses.

Optimum Conditions.

(1) The molasses had an original solids content of 80° Brix. Runs were made in which the molasses was diluted to Brix solids varying between 45° and 60°. If the dilution was too great, the concentration of aconitic acid in the resulting solution was low and the yield of aconitate was decreased. If the dilution was not great enough, the solution foamed when heated. The results obtained in the preliminary runs in the pilot-plant indicated that the process works best when the dilution is such that the solution has a concentration of 50° to 55° Brix solids. This concentration is satisfactory for returning the treated molasses to the sugarhouse for further processing by usual procedures.

(2) The pH of the original molasses was about 5.5, which is too low for maximum precipitation of aconitate. Experiments in which the pH was adjusted with magnesium oxide, with calcined magnesite, with potassium hydroxide, with sodium hydroxide and with calcium oxide or hydroxide indicated that calcium oxide or hydroxide was the best agent for the purpose. The optimum pH was found to be 6.5 to 6.8; greater alkalinity caused the solution to foam when heated. The lime used should contain a minimum of carbonate since the carbon dioxide liberated causes the solution to foam badly.

(3) Calcium chloride and magnesium chloride of technical grades were used to increase the calcium and magnesium contents of the solution. The quantities were varied until it was found that the most satisfactory results were obtained by adding a solution containing three parts of anhydrous calcium chloride and one part of anhydrous magnesium chloride for every five parts of aconitic acid in the solution. These were the least amounts required. Larger quantities had no effect on the aconitate recovery, but increased unnecessarily the percentage of ash and of chlorides in the molasses returned to the sugarhouse.

(4) The molasses was always diluted and limed and then heated to 120° F. before the solution of the chlorides was added. The aconitate began to separate at about 180° F. but best results were obtained at temperatures between 200° and 210° F. Temperatures above 210° F. caused decomposition and foaming of the molasses.

(5) The temperature must be held at 200° F. for at least 45 minutes. Holding the temperature beyond one hour had very little effect on the recovery of the aconitate. When it was desired to allow the aconitate to

settle, heating was stopped and the temperature was allowed to fall during the settling period.

(6) It was impossible to filter the aconitate from the molasses. The presence of large proportions of the amorphous, slimy material made separation of the aconitate by settling and decantation very unsatisfactory, because the amorphous matter prevented the aconitate from sinking and packing. The problem of separation was satisfactorily solved by centrifuging the whole batch, or allowing the aconitate-amorphous mixture to settle as well as it would and then decanting as much of the supernatant molasses as possible and running the bottom slurry through the centrifuge. By using a 14-inch solid basket rotating at 1500 r.p.m. the aconitate was thrown out of suspension as a cake while most of the amorphous matter remained in suspension. The cake of aconitate was then dropped into hot water, mixed into a slurry and again passed through the centrifuge at 1500 r.p.m. The water from this centrifuging, called hereafter the "wash water", contained sugar and the smallest crystals of aconitate and was returned to the process as the water for diluting the molasses and dissolving the chemicals for the next batch, thus conserving the sugar and supplying seed crystals of aconitate for the new crop.

Summary of Recoveries of Aconitate.

The optimum conditions were worked out in 33 exploratory runs, for the first 2 of which 37.4 gallons of molasses were used, while for the remaining 31 runs the amount was cut to 15 gallons per run. Modifications of the apparatus were made as the work progressed and as the results obtained indicated the need for improvements. Following the exploratory runs, the optimum conditions found were applied to 16 runs using 30 gallons each. Data on the

49 runs are given in Table III.

No separation of the precipitated aconitate was made in 2 of the 33 exploratory runs. The remaining 31 runs, in which a total of 510 gallons of molasses, representing 51 tons of cane, were used, yielded 112.4 lbs. of crude aconitate. The minimum recovery in this series was 7.6% of aconitic acid in the molasses, and the maximum was 48.5%. Distribution was as follows: Recoveries from 15 runs were less than 30%; from 2 runs, between 30 and 35%; from 8 runs, between 35 and 40%; from 3 runs between 40 and 45%; and from 3 runs, between 45 and 50%.

In the second series of 16 runs using the optimum conditions, a total of 480 gallons of molasses, representing 48 tons of cane, yielded 107.8 lbs. of crude aconitate. The minimum recovery here was 18.2% of aconitic acid in the molasses, and the maximum was 56.8%. Distribution was: Recoveries from 3 runs were less than 30%; from 3 runs, between 30 and 35%; from 2 runs, between 35 and 40%; from 2 runs, between 40 and 45%; from 3 runs, between 45 and 50%; and from 3 runs, in excess of 50%.

The crude aconitate from the first series varied in composition from 29.3% aconitic acid as the minimum to 61.8% as the maximum (this maximum of aconitic acid content was obtained in a run which gave very low recovery - a sacrifice of yield and recovery for high purity aconitate). In the second series of runs the variation in composition was less, the minimum being 48.0% and the maximum 56.0% aconitic acid.

The total aconitate recovered from 7 identical consecutive runs of 30 gallons each, i.e., from 210 gallons of molasses (or 21 tons of cane) weighed 56.8 lbs., and, when composited, was found to contain 56.0% of aconitic acid. These figures indicate a recovery of 46% of the aconitic acid originally present in the molasses. It is emphasized that all of the above results on optimum conditions and yields were those found applicable to the particular batch of molasses obtained from this factory near the end of the grinding season. Turbinado sugars were being manufactured. Conditions and yields for molasses obtained from other mills, differently operated, could be expected and, in fact, have been found to vary.

Table III

RECOVERY OF CALCIUM MAGNESIUM ACONITATE FROM SUGARCANE "B" MOLASSES

DATA SHEET

Original Molasses

Sample No.	Brix	Ca % Brix	Mg % Brix	Acon. Acid % Brix
1	80.2	0.56	0.20	3.80
2	80.3	0.56	0.20	3.50
3	80.7	0.51	0.16	3.56
4	80.2	0.51	0.25	3.94

Treated Molasses

Run	Brix	Alkali Used	pH Initial	pH Final	CaCl$_2$ a/ Added Grams	MgCl$_2$ b/ Added Grams	Settling	Yield Lbs.	Acon. Acid in Precipitate %	Recovery %
Batches of 37.4 gal. each										
1	65.0	MgO c/	6.1	6.1	6478	800	poor	7.4^S	41.20	22.9
2	65.0	"	5.9	5.5	6478	158	"	6.5	39.15	19.1
Batches of 15 gal. each.										
3	68.0	MgO	6.7	5.5	3175	160	fair	0.43^F	not det.	not det.
4	60.5	"	6.9	5.8	3175	175	poor	4.37^S	33.30	26.8
5	56.6	Mag'site c/	6.0	6.0	3175	1362	fair	7.25^S	37.20	46.4
6	58.6	"	6.4	5.8	2400	545	poor	5.12^S	36.50	38.6
7	64.3	"	6.3	5.5	2400	545	"	2.5^S	29.29	26.8
8	51.1	"	6.4	5.7	2400	554	"	4.56^S	45.6	39.2
9	48.7	"	6.4	5.7	2400	554	fair	3.0^S	38.3	41.2
10	56.3	NaOH	6.5	-	2400	1478	"	4.81^S	45.8	41.5
11	56.1	KOH	6.5	5.6	2400	1478	"	3.87^S	32.2	23.5
12	54.5	"	6.3	5.4	2400	1478	"	3.75	42.3	29.8
13	53.5	Ca(OH)$_2$CP	6.6	5.6	2400	1478	poor	6.69^S	37.5	47.2
14	54.7	Ca(OH)$_2$ d/	6.6	5.9	2400	700 b/	fair	3.31	44.66	27.8
15 e/	55.0	"	6.3	6.1	2400	700	"	3.94	48.14	36.5
16	53.1	"	6.5	6.3	1200	700	none	2.88	45.82	25.5
17	49.5	"	6.3	6.0	1800	700	fair	2.25	50.46	21.8
18	52.1	"	6.5	6.0	2400	700	"	not determined		

Table III (Cont'd.)

RECOVERY OF CALCIUM MAGNESIUM ACONITATE FROM SUGARCANE "B" MOLASSES

DATA SHEET

Treated Molasses

Run	Brix	Alkali Used	pH		$CaCl_2$ a/ Added	$MgCl_2$ b/ Added	Settling	Yield	Acon. Acid in Precipitate	Recovery
			Initial	Final						
					Grams	Grams		Lbs.	%	%
Batches of 15 gal. each.										
19	52.0	$Ca(OH)_2$ d/	6.3	6.4	2400	700	fair	not det.	55.36	--
20	54.8	"	6.5	6.0	2000	700	good	3.96	51.91	39.4
21	52.0	CaO(CP)	6.0	6.0	2000	350	fair	2.38	56.55	27.5
22	51.7	"	6.1	6.1	1800	400	poor	3.1	56.00	35.4
23	53.9	"	6.1	6.1	2000	500	fair	3.2	58.00	36.7
24	54.9	"	6.2	6.2	2000	700	good	3.6	52.50	38.6
25	60.4	"	6.3	6.3	2000	700	none	3.55	55.97	40.1
26 f/	57.2	"	6.3	6.3	2000	700	good	2.71	57.09	31.6
27 g/	58.6	"	6.5	6.3	2000	1000	none	2.6	52.50	27.8
28	55.8	"	6.9	6.4	2000	1000	"	4.66	51.04	48.5
29 gh/	56.0	"	6.9	6.2	2000	1000	very good	2.34	58.25	27.8
30 gh/	50.3	"	6.9	6.2	2000	1000	" "	0.70	53.10	7.50
31 gh/	43.2	"	6.9	6.2	2000	1000	" "	1.43	61.77	18.0
32 g/	54.7	"	6.4	5.6	2000	1400	none	3.3	55.00	37.0
33	55.9	"	6.3	5.7	2000	1400	very good	3.1	54.56	30.8
Batches of 30 gal. each										
34 g/	k/	CaO(CP)	6.3	-	4000	2000	m/	5.6 n/	63.5 n/	32.6
35	"	"	6.7	-	4000	2000	"	6.4 n/		41.6
36	"	"	6.5	-	4000	2000	"	7.1 n/	63.07 n/	45.7
37	"	"	6.3	-	4000	2000	"	7.1 n/		45.7
38 g/	"	"	6.7	-	4000	2000	"	3.45	51.71	16.2
39	"	"	6.2	-	4000	2000	"	5.00	51.71	26.4
40 g/	"	"	6.2	-	4000	2000	"	3.7 n/	47.93 n/	18.2
41 g/	"	"	6.5	-	4000	2000	"	6.3 n/	50.89 n/	32.8
42 g/	"	"	6.6	-	4000	2000	"	6.3 n/		32.8
43 g/	"	"	6.8	-	4000	2000	"	6.69		38.4
44	"	"	6.8	-	4000	2000	"	8.81		50.5
45	"	"	6.8	-	4000	2000	"	8.98		51.5
46	"	"	6.8	-	4000	2000	"	9.88	56.02	56.5
47 g/	"	"	6.8	-	4000	2000	"	8.50		48.7
48	"	"	6.8	-	4000	2000	"	7.15		41.0 p/
49	"	"	6.8	-	4000	2000	"	6.78		39.8 p/

Table III (Cont'd.)

a/ Commercial grade, 75% $CaCl_2$ was used throughout.

b/ For Runs 1 through 13, crystalline $MgCl_2.6H_2O$ was used. For the remaining runs commercial grade "flake" magnesium chloride (50% $MgCl_2$) was used.

c/ For Runs 1 through 4 MgO of C.P. grade was used; for Runs 5 through 9, commercial calcined magnesite was used.

d/ For Runs 14 through 20 inclusive, commercial hydrated lime was used, but it contained so much carbonate that the batch foamed excessively.

e/ Beginning with Run 15, the wash from a previous run was used for dilution of the molasses, solution of the chlorides, and preparation of the milk of lime, except as indicated (footnote g/).

f/ This batch was heated only to 185 to 190° F. instead of to 200 to 210° F.

g/ Fresh water used for dilution, etc., instead of wash water from a previous run.

h/ Molasses was previously treated to remove the amorphous material before precipitating the aconitate.

k/ Dilutions were such that the final Brix should be 55.0, but the Brix was not determined.

m/ In Runs 34 through 49 the aconitate was collected in the centrifuge without waiting for it to settle.

n/ These products were dried at 140° C. instead of 75° C.

p/ Original molasses was frothing badly, hence 30 gallons here represent less, on a weight basis, than in the proceeding runs.

F indicates that an attempt was made to collect the aconitate on a filter press.

S indicates that the aconitate was collected in a supercentrifuge. The yield values which are not marked S or F are for aconitate collected on the 14" solid-basket centrifuge.

Aconitic Acid Balance.

The weight of aconitic acid left in the dilute molasses from the centrifuge, plus that in the wash from the centrifuge, plus that in the aconitate recovered should equal the weight of aconitic in the original batch of molasses plus that introduced in the wash water from the previous run. This balance serves as a check on mechanical losses such as spillage and incomplete removal of the aconitate from the apparatus. Table IV gives the balances obtained in 10 of the exploratory runs and indicates that the mechanical losses were generally small. With larger-scale operations the balance should be more nearly perfect.

Talbe IV

ACONITIC ACID BALANCE

Weights are approximations to the nearest 0.1 lb.

Run No.	Input			Output			
	Molasses	Wash	Total	Molasses	Wash	Aconitate	Total
	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.	Lbs.
14	4.9	0.0	4.9	2.8	0.4	1.5	4.7
20	4.9	0.4	5.3	3.0	0.4	2.1	5.5
21	4.9	0.4	5.3	3.6	0.5	1.4	5.5
22	4.9	0.5	5.4	3.4	0.4	1.8	5.6
23	4.9	0.4	5.3	3.0	0.4	1.9	5.3
24	4.9	0.4	5.3	3.1	0.4	1.9	5.4
25	4.9	0.4	5.3	2.7	0.4	2.0	5.1
27	4.9	0.4	5.3	2.8	0.4	1.3	4.5
28	4.9	0.4	5.3	2.5	0.4	2.4	5.3
33	4.9	0.4	5.3	2.7	0.3	1.7	4.7
Av.			5.3				5.1

CONVERSION OF THE ACONITATE TO ITACONIC ACID

Pilot-Plant Experiments.

The aconitate was dried and pulverized for use in the pilot-plant study of the decarboxylation to itaconic acid. These studies centered on (1) the concentration of aconitate, (2) the optimum pH (3) the duration of the decarboxylation, (4) extent of isomerization to citraconic acid, and (5) recrystallization of the crude itaconic acid.

Optimum Conditions.

(1) The best concentration was the same as found in the laboratory experiments, i. e. a slurry consisting of 20% by weight of the crude aconitate.

(2) The optimum pH was found to be from 2.0 to 2.5. Within this range no significant change in duration of heating could be noted in the apparatus used. Above and below this range it was noted that the time elapsed before cessation of the evolution of carbon dioxide became greater.

(3) At 135° to 140° C. (275° to 285° F.) and pressure of 32 to 34 lbs., the decarboxylation of slurry having pH 2.0 to 2.5 was complete in approximately one and one-half hours. Heating should not be continued after the decarboxylation has become complete.

(4) The magnesium in the crude aconitate caused some isomerization of the itaconic acid to citraconic acid. Analysis of the mother-liquor from the first crop of itaconic acid showed that it contained citraconic acid to the extent of about 6% of the total theoretical yield of decarboxylated products. No satisfactory means of overcoming this isomerization has been found.

(5) The recrystallization of the crude itaconic acid offered some

difficulty at first, since the magnesium sulfate and coloring matter in the crude acid interfered with the working up of mother liquors. By means of the method developed and described later 87% of the crude itaconic acid was recovered as white crystals melting at 162-164° C.

Summary of Yields and Recoveries of Itaconic Acid.

The above optimum conditions were worked out in a total of 31 runs. The conditions adopted were used in 8 of these runs, each on 4.2 lbs. of crude aconitate averaging 55% aconitic acid. The average production of crude itaconic acid from these 8 runs was 76% of the theoretical, with the minimum of 73% and maximum of 77%. In these runs a total of 33.6 lbs. of the aconitate gave 10.5 lbs. of crude itaconic acid having a tan color and melting at around 157° C. By the recrystallization technic (which was not completely developed until after the first half of these runs had been made) 87% of the weight of the crude itaconic acid was obtained as white crystals melting at 162-164° C. This percentage recovery, applied to the 10.5 lbs. of crude acid, would have given 9.1 lbs. of purified acid, which is 66% of the amount of itaconic acid theoretically equivalent to the aconitate. The percentage recovery in the crystallizations can no doubt be increased in larger batches, at least in part, by cutting down mechanical losses through use of more efficient equipment. It is also possible that the best technic for the crystallizations was not found in these experiments.

The citraconic acid produced should be added in determining the total yield of decarboxylated product. The citraconic acid produced in these experiments was not isolated as such, but it is possible that its recovery would be worth while in large-scale production, since it also has application in the production of plastic products.

The decarboxylation process for itaconic acid should be studied on a much larger scale with special attention to the crystallization processes. This study has shown that the decarboxylation itself is feasible and that the main points for further study concern the isolation and purification of the acid, and possibly the recovery of the citraconic acid formed during the reaction.

THE PROCEDURES IN DETAIL

I. The Production of Calcium-Magnesium Aconitate.

Apparatus. The apparatus used in the pilot-plant for the recovery of the aconitate from B molasses consisted essentially of 4 tanks and a centrifuge assembled and equipped with accessories as sketched in Figure 1.

DILUTION TANK (1) had a capacity of 60 gallons and was equipped with a short STEAM COIL (A) and a stirrer driven by MOTOR (B). This tank had a bottom outlet for discharging its contents into REACTION TANK (2) by gravity.

SOLUTION TANK (3) had a capacity of 15 gallons and a bottom outlet for discharging its contents by gravity in REACTION TANK (2).

REACTION TANK (2) with conical bottom had a capacity of 75 gallons. It was equipped with four SIGHT GLASSES (K), one located in the side of the cone, the remaining three at equal distances apart on the side of the tank, and with five DECANTATION OUTLETS (D), one from the side of the cone, the remaining four at 4-inch intervals up the side of the tank from the top of the cone. The tank was heated by two STEAM COILS (F) and (H), one above the other and individually controlled, the bottom one by a THERMOSTATIC AUTOMATIC VALVE (E). A single turn of perforated STEAM COIL (N) was located just below the top of the cone to provide means of agitation by steam blow-up. The temperature of the batch was measured by the RECORDING THERMOMETER (C). This tank also had a bottom discharge leading to PUMP (L) or to the drain.

PUMP (L) lifted the slurry from REACTION TANK (2) to the SLURRY TANK (5) which had a capacity of 35 gallons and was equipped with MOTOR DRIVEN STIRRER (L). It had a bottom outlet for feeding the slurry by gravity into the 14-inch solid basket of the CENTRIFUGE (6).

SUPPLY TANK (4) was a barrel or drum of molasses supported on a movable wooden horse.

Proportionate Quantities of Materials.

30 gallons of 80 Brix B molasses.

14 oz. (400 grams) of lime.

8 lbs. 13 oz. (4 kilograms) of commercial anhydrous calcium chloride containing 75% of actual $CaCl_2$.

4 lb. 6-1/2 oz. (2 kilograms) of flake magnesium chloride containing 50% of actual $MgCl_2$.

20 gallons of water, preferabl the wash water from a previous run.

Procedure.

The procedure developed for recovering the aconitate from this type of molasses is represented diagrammatically in Figure 2.

Thirty gallons of the B molasses was drawn from drum (4) into the dilution tank (1) and mixed with 10 gallons of the wash water discharged from the centrifuge in a previous run. The use of the wash water in this way served the purposes of conserving the sugar dissolved in it and of using the small crystals of aconitate suspended in it as seed for the new batch of aconitate. Since, in the sugar mill, the molasses would enter the process at a somewhat elevated temperature, the diluted molasses in tank (1) was heated to a temperature of 120° F. While it was coming to this temperature, 400 grams of calcium oxide was mixed with 4 gallons of wash water from the previous run and the milk of lime so produced was mixed with the solution of molasses in tank (1) to raise the alkalinity of the solution to a pH of at least 6.5 but not over 6.8. Meanwhile 4 kilograms of commercial calcium chloride (75% $CaCl_2$) and 2 kilograms of flake magnesium chloride (50% $MgCl_2$) were dissolved in solution tank (3), in 6 gallons of the wash water from the previous run.

When the diluted molasses in tank (1) had attained the temperature of 120° F., the outlets of tanks (1) and (3) containing the molasses and the solution of the chlorides, respectively, were opened and both solutions were discharged into reaction tank (2) simultaneously and at such rates that both tanks were emptied at approximately the same moment. This control of the rates of discharge aided the rapid mixing of the two solutions of differing densities to form a final solution of approximately 55 Brix. Further and final mixing was effected by blowing steam into the mixture through coil (N) while the temperature of the mixture was being raised to 210° F. This method of mixing and agitation in the reaction tank produced larger crystals of the aconitate than when more violent agitation with a mechanically operated stirrer was employed. The temperature was raised as rapidly as possible to 200-210° F. and held within this range for at least 45 minutes, more generally for one hour, with an occasional gentle blow-up with steam.

The heating was then stopped and the precipitate was allowed to settle for another hour. (In some runs, this settling period was omitted, and the whole batch was sent directly to the centrifuge.) The clear supernatant dilute molasses was then drawn off through that one of the decantation outlets (D) which was immediately above the layer containing the precipitate as determined by observing the clarity of samples withdrawn from the various outlets. The thin slurry remaining in the reaction tank (2) was then discharged through the pump (L) into the slurry tank (5). Here it was kept in agitation while it was fed by gravity into the solid 14"-basket centrifuge (6), operated at a speed of 1500 r.p.m. The molasses from the centrifuge was caught in drums and united with that decanted from the reaction tank. Its quality was such that it could be used directly in the usual sugarhouse procedures for the crystallization of sugar.

The cake of aconitate in the basket of the centrifuge was suspended in 20 gallons of hot water and the resulting slurry was pumped back into the slurry tank (5) from which it was again fed to the centrifuge as before. The water from this centrifuging was used as described for diluting the molasses and dissolving the chemicals needed for the next batch. The washed cake was dried at 165° to 170° F. and then pulverized.

II. The Production of Itaconic Acid from the Aconitate.

Apparatus. The reaction was carried out in an electrically heated, glass-lined pressure kettle of 5-gallon capacity, tested for 35 lb. pressure, and equipped with a motor-driven stirrer and a water-cooled reflux condenser. Pressure gage and safety pop-valve were attached at the top of the condenser. Also attached to the top of the condenser was a back-pressure regulator (McAlear #312) set to hold the pressure between 32 and 34 lbs. The temperature of the reaction was determined by a thermocouple inserted in the hollow shaft of the stirrer.

Large earthenware Buchner filters were used for separating calcium sulfate from the acid reaction mixtures. Concentration of the solutions was carried out in large size laboratory glassware under reduced pressure. The concentrated solutions were allowed to crystallize in large glass beakers.

Proportionate Quantities of Materials.

4.2 lbs. of calcium-magnesium aconitate (55% aconitic acid).

2.54 lbs. (625 cc.) of concentrated sulfuric acid, added in two parts, one of 2.03 lbs. (500cc.) and one of 0.51 lbs. (125 cc.).

2.25 gallons of water.

0.25 lbs. of decolorizing carbon.

Procedure.

The procedure for decarboxylating the aconitate to itaconic acid is represented diagrammatically in Figure 3.

Four and two-tenth pounds of the calcium-magnesium aconitate, averaging about 55% aconitic acid, were slurried with 2.25 gallons of water and 2.03 lbs. (500 cc.) of concentrated sulfuric acid were added with stirring. This produced a slurry having a pH of 2.0 to 2.5 and containing calcium and magnesium sulfates, calcium and magnesium aconitates and aconitic acid, but no free sulfuric acid. The slurry was heated with stirring in the pressure vessel to 135° C. (275° F.). At about 100° C. (212° F.) the evolution of carbon dioxide became evident from the rapid increase in pressure in the vessel. The pressure was allowed to rise to 33-34 lbs. before releasing gas. If the back pressure regulator (or other automatic device) was not used, the pressure was controlled by manual operation of the valve at the top of the reflux column. The temperature was held at 135° C. (275° F.) and the pressure at 32 - 34 lbs. for one and one-half hours, when no further increase in the pressure indicated that the decarboxylation reaction was at an end. Then the heating was stopped and the apparatus was allowed to cool for one-half hour before the kettle was opened. The remaining 0.51 lb. (125 cc.) of concentrated sulfuric acid and 0.25 lb. of decolorizing carbon were added and the whole thoroughly mixed. This amount of sulfuric acid was a slight excess over that required to combine with the small amount of calcium and magnesium aconitates left when the first addition of sulfuric acid was made.

The mixture was filtered hot on the Buchner funnel and the precipitate of calcium sulfate and carbon was slurried with one quart of hot water and filtered again. The combined filtrates amounted to about 2.5 gallons of solution containing itaconic acid, sulfuric acid, some citraconic acid, magnesium sulfate and some calcium sulfate. This solution was evaporated under reduced pressure to about one-fourth its original volume (i.e. to about 2.5 quarts) and then cooled rapidly with stirring. After it had been kept at low temperature for two hours the itaconic acid which had crystallized was collected on a Buchner funnel and the filtrate was concentrated under reduced pressure to about one-half its volume (i.e. to about 1 to 1-1/2 quarts). This was cooled rapidly with stirring and kept cold for 2 hours when a second crop of crystals of itaconic acid was obtained. By allowing the filtrate from this second crop to stand over night a small third crop could be obtained, but this crop was so badly contaminated with magnesium sulfate and coloring matter that it was not worked up with the other crops, and is not included in the yields of itaconic acid given here.

The crystals were light tan in color, melted around 157° C. and were purified by recrystallization. One pound of the crude crystals were dissolved in a quart of the mother liquor from a previous recrystallization and 50 grams of carbon were added. The whole was heated on the steam bath at 80-90° C. for one-half hour. The carbon was removed by rapid filtration and washed with 100 cc. of hot water. The combined filtrate and washing was cooled rapidly with stirring and kept cool for 2 hours. The itaconic acid separated in white crystals which melted at 162-164° C. When the filtrate from these crystals was allowed to stand over night a small amount of slightly colored crystals of itaconic acid was obtained. It was not practical to evaporate this filtrate for a further crop of crystals since the solution darkened during the concentration and the crystals obtained were highly colored and could not be purified in satisfactory manner, the color being tenaciously retained or new color being developed during the recrystallization. Greatest conservation and maximum recovery were obtained by employing the mother liquors from a previous recrystallization, decolorized with carbon if very dark in color, for the solvent in the new recrystallization, rather than by concentrating the mother liquors as in ordinary recrystallization technics.

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ADDENDA

THE REMOVAL OF MAGNESIUM FROM ALKALINE-EARTH ACONITATE

The alkaline-earth aconitate which is obtained from molasses may be crystalline in form or it may be amorphous (14). The factors which determine the form in which it separates are not known. If it separates in the crystalline form it is possible to remove the magnesium from the material and to obtain crystalline tricalcium aconitate. Amorphous calcium-magnesium aconitate, however, does not respond to the treatment.

The calcium-magnesium aconitate, whether crystalline or amorphous, has the composition of a hexahydrate of the type $Ca_2MgAcon_2.6H_2O$. When the crystalline compound is heated at 140° C. for several hours, it loses two-thirds of the water of crystallization or hydration and disintegrates into a fine powder, which has the empirical composition $Ca_2MgAcon_2.2H_2O$, (14) and therefore hereafter will be called the dihydrate. The original hexahydrate behaves like a chemical individual in that it has definite and characteristic crystal form and cannot be separated into simpler salts, such as tricalcium aconitate hexahydrate and trimagnesium aconitate hexahydrate, by leaching with water or other solvent (15). The dihydrate, however, behaves like a physical mixture of lower hydrates of tricalcium aconitate and trimagnesium aconitate from which the latter, being very soluble, may be removed by leaching or may be reacted in situ with calcium chloride solution to form insoluble tricalcium aconitate and soluble magnesium chloride. The latter passes into solution and may be completely washed away from the calcium aconitate. During the reaction the dihydrate takes up one molecular proportion of water to form the stable trihydrate of tricalcium aconitate. The net overall result is the transformation of the hexahydrate of calcium-magnesium aconitate to the trihydrate of tricalcium aconitate:

$$Ca_2MgAcon_2.6H_2O + CaCl_2 \rightarrow Ca_3Acon_2.3H_2O + MgCl_2 + 3H_2O.$$

When the amorphous form of calcium-magnesium aconitate is heated at 140° C., it also loses about two-thirds of its water of hydration, but it does not disintegrate, and when treated with water or with calcium chloride solution the only reaction produced is rehydration with the evolution of heat. There is no replacement of magnesium by calcium during the process and amorphous hexahydrate of the same composition as the original aconitate is recovered.

The apparatus needed for this process consists of a drying oven regulated for holding the temperature of 140° C. (285° C.), a slurrying vessel equipped with a mechanical stirrer, and a filter. The slurry vessel and filter must be made of material resistant to strong, hot calcium chloride solutions.

The only chemical needed is anhydrous calcium chloride. The chloride solution filtered from one batch of aconitate may be used by reheating for treatment of second and third batches of aconitate.

The essential points in working the process have been found to be (1) dehydration, (2) concentration, (3) temperature of the calcium chloride solution, and (4) agitation and mixing.

(1) The dry, crystalline calcium-magnesium aconitate must be heated to at least 140° C. for a sufficient length of time to remove 9 to 12% (depending on the purity of the aconitate) of its weight, or until it has come practically to constant weight. It should be completely disintegrated to a fine powder so that no gritty particles are felt when it is rubbed between finger and thumb.

(2) The magnesium is most effectively removed by solutions containing 20 to 40% of anhydrous calcium chloride. Weaker solutions are too quickly exhausted and stronger solutions have a solvent action on the aconitate, resulting in large losses of material.

(3) The solution of calcium chloride should be hot (100° C. or higher) and the slurry should be maintained at from 90° to 100° C. throughout the treatment. At temperatures below 80° C. rehydration of the dihydrate to hexahydrate takes place with only partial displacement of the magnesium.

(4) The dihydrate must be quickly and thoroughly slurried with the calcium chloride solution, and the slurry must be agitated throughout the reaction period. Since the dihydrate often has a high resistance to wetting, this slurrying may be difficult. The best means of doing this operation was not found in the few runs which were made on the process.

The Procedure.

The dihydrate was slurried with the hot calcium chloride solution and kept in agitation for 30 minutes while the temperature was maintained at 90° to 100° C. The hot slurry was then filtered rapidly on Buchner funnels. The filtrate was reheated to 100° to 105° C. and used to make a slurry with a new batch of the dihydrate, which was treated in exactly the same way. The aconitate on the filter was washed with hot water to remove chlorides, dried at 100° to 105° C. and used for decarboxylation to itaconic acid. The filtrate from the second slurry was heated and used for a third. The filtrate from the third slurry was discarded in these experiments.

The details and data obtained are given in Table V. The process was not studied further because it did not seem to be economical since the large amounts of calcium chloride needed and the large volumes of wash water obtained in removing the chlorides from the aconitate could not be satisfactorily integrated into the itaconic acid process, at least at this time. The table shows that the magnesium can be eliminated by this procedure, if for any reason it is desired to produce a magnesium-free aconitate, but that the process is expensive. While further study of the process would be desirable, it was not expedient to carry on the work, especially as it can be applied only to crystalline calcium-magnesium aconitate and not to the amorphous variety which is obtained from the molasses made in some sugar mills.

Table V

ELIMINATION OF MAGNESIUM FROM CRYSTALLINE CALCIUM-MAGNESIUM ACONITATE

Exp. No.	Wt. Treated	$CaCl_2$ Solution (a) Wt. in Vol. Water	Loss in Wt. %	Mg in Product %
Av. original aconitate		--	-	2.44
" heated aconitate		--	-	2.76
1 A	400 gm	1920 gm in 6 liters	15.5	2.07 (b)
1 B	" "	Filtrate from 1 A	13.5	0.53
1 C	" "	" " 1 B	6.75	0.71
2 A	" "	1920 gm in 6 liters	19.5	0.29
2 B	" "	Filtrate from 2 A	0.0	0.44
2 C	" "	" " 2 B	0.0	0.77
3 A	800 gm	3800 gm in 5.5 liters	16.4	0.57
3 B	" "	Filtrate from 3 A	24.5	0.13
3 C	" "	" " 3 B	6.5	2.29 (c)
4 A	5 lbs.	24 lbs. in 4.1 gals.		0.74
4 B	" "	Filtrate from 4 A	10	0.31
4 C	" "	" " 4 B		0.25
5 A	6 lbs.	28 lbs. in 4.9 gals.	2.0	0.42
5 B	" "	Filtrate from 5 A	5.0	0.00
5 C	" "	" " 5 B	7.0	0.25
6 A	" "	28 lbs. in 4.9 gals.	7.0	0.00

(a) Weights are for commercial anhydrous $CaCl_2$, 75% actual $CaCl_2$; the remaining 25% was assumed to be water, and in figuring concentration of the chloride, the water contained in the chloride was added to the water given in the table.

(b) In this experiment, the calcium chloride and the aconitate were mixed dry and slurried with hot water, resulting in rehydration of a large part of the dihydrate before the calcium chloride could dissolve and enter into reaction.

(c) In this experiment the temperature was too low and rehydration of the dihydrate resulted.

ANALYTICAL METHODS

I. Rapid Method for Determination of Calcium in Molasses. (16).

Reagents: Dilute ammonium hydroxide - concentrated ammonium hydroxide diluted with 3 volumes of water.

Dilute hydrochloric acid - concentrated hydrochloric acid diluted with 3 volumes of water.

0.5 N ammonium oxalate.

Determination.

Weigh into a platinum or porcelain crucible such an amount of the molasses as will contain 5 to 8 grams of solids. Char and burn it free from carbon. Dissolve the ash in dilute hydrochloric acid and add dilute ammonium hydroxide until the solution is just alkaline to congo red paper (pH 4.5 - 5.0). Filter and wash the filter paper several times with small portions of water. The volume of the solution and combined washings should be about 150 ml. Add 60 ml. of hot ammonium oxalate solution and make faintly alkaline to litmus paper with dilute ammonium hydroxide. Allow the precipitate to stand 30 minutes. Filter on tared Gooch crucible and wash with small portions of water. Save the filtrate and washing for the determination of magnesium. Dry the precipitate for 2 hours at 100° to 105° C. Cool and weigh as $CaC_2O_4.H_2O$. Factor for conversion to Ca = 0.2739.

II. Rapid Method for the Determination of Magnesium in Molasses. (17)

Reagents: Dilute ammonium hydroxide - concentrated ammonium hydroxide diluted with 3 volumes of water.

Concentrated ammonium hydroxide.

Solution of 8-hydroxyquinoline - 12.5 grams of 8-hydroxyquinoline dissolved in 30 ml. of glacial acetic acid and then diluted with water to one liter.

Determination.

Make the filtrate from the calcium determination definitely ammoniacal with dilute ammonium hydroxide and heat to 60° - 70° C. Add an excess of the 8-hydroxyquinoline solution (25 to 30 ml.) and 4 ml. of concentrated ammonium hydroxide. Stir vigorously for 10 minutes and then allow to settle. Filter on a tared Gooch crucible and wash several times with hot dilute ammonium hydroxide. Dry the precipitate at 100° to 105° C. for 2 hours. Cool and weigh as $Mg(C_9H_6NO)_2.H_2O$. Factor for conversion to Mg = 0.06938.

III. Determination of Aconitic Acid in Molasses. (18). Note that the method depends on the accurate determination of carbon dioxide, for which either a gravimetric or volumetric method may be used.

Reagents:

Saturated solution of neutral lead acetate.

Suspension of acid-washed asbestos.

Acetone.

Dry potassium acetate crystals.

Glacial acetic acid.

Apparatus:

Beaker - 400 ml.

Small Buchner or Hirsch funnel and suction flask.

2 Calcium chloride tubes charged with soda-lime or Ascarite.

250-ml. Erlenmeyer flask.

Reflux condenser.

Claissen-type adapter.

Gas washing bottle.

Carbon dioxide absorption train, (19).

Determination.

Weigh into the beaker sufficient molasses to give 20 to 30 grams of solids, and dilute with water to about 200 ml. Mix and heat on the steam bath to about 80° to 90° C. Add with stirring 50 ml. of saturated lead acetate solution. Allow the precipitate to settle. Flute a strong filter paper to fit the small Buchner or Hirsch funnel and deposit a thin layer of asbestos uniformly over the filtering area. Collect the lead precipitate on the prepared filter and police from the beaker with water. Wash the precipitate once with water and drain the water away by suction as completely as possible. Stop the suction and fill the filter paper with acetone. Puddle the precipitate gently in the acetone to insure thorough penetration of acetone through the whole precipitate. Remove the acetone by suction and repeat with a second batch of acetone. Continue the suction after the second washing with acetone until the odor of acetone has completely gone from the paper and precipitate when suction is stopped. Dry the paper and precipitate in the oven at 120° C. for 30 minutes.

Introduce the paper and precipitate into the Erlenmeyer flask with 10 grams of potassium acetate crystals and some boiling chips and cover with 100 ml. of glacial acetic acid. Through a one-hole rubber stopper fitted in the top of the straight arm of the Claissen adapter pass a glass tube so that the end of the tube is about one-quarter inch above the surface of the acetic acid. Connect to the other end of this tube one of the tubes charged with soda-lime or Ascarite. Connect the side arm of the Claissen adapter with the reflux condenser and by rubber tubing connect the top of the condenser with the inlet tube of the gas washing bottle containing distilled water to a depth of at least 4 inches.

Connect the soda-lime or Ascarite tube with a source of compressed air and in order to sweep out carbon dioxide pass a stream of air slowly through the apparatus for 20 to 30 minutes at the rate of about 120 to 180 bubbles per minute in the washing bottle. Prepare the carbon dioxide absorption train and, when the carbon dioxide has been removed from the apparatus, attach it to the outlet tube of the washing bottle. Attach the other Ascarite or soda-lime tube to the other end of the absorption train. Continue the stream of air and heat the mixture in the Erlenmeyer flask to boiling. Boil for an hour and a half under reflux, then allow the reaction mixture to cool slowly for 30 minutes while the current of air is continued. Disconnect the absorption train and determine the carbon dioxide absorbed. Multiply the grams of carbon dioxide by 3.9545 to obtain the equivalent amount of aconitic acid.

IV. Determination of Aconitic Acid in Aconitates.

Weigh into the Erlenmeyer flask 2 grams of the dry aconitate. Add 10 grams of potassium acetate and some boiling chips and 100 ml. of glacial acetic acid, assemble the apparatus and proceed with the decarboxylation and absorption of carbon dioxide exactly as described above.

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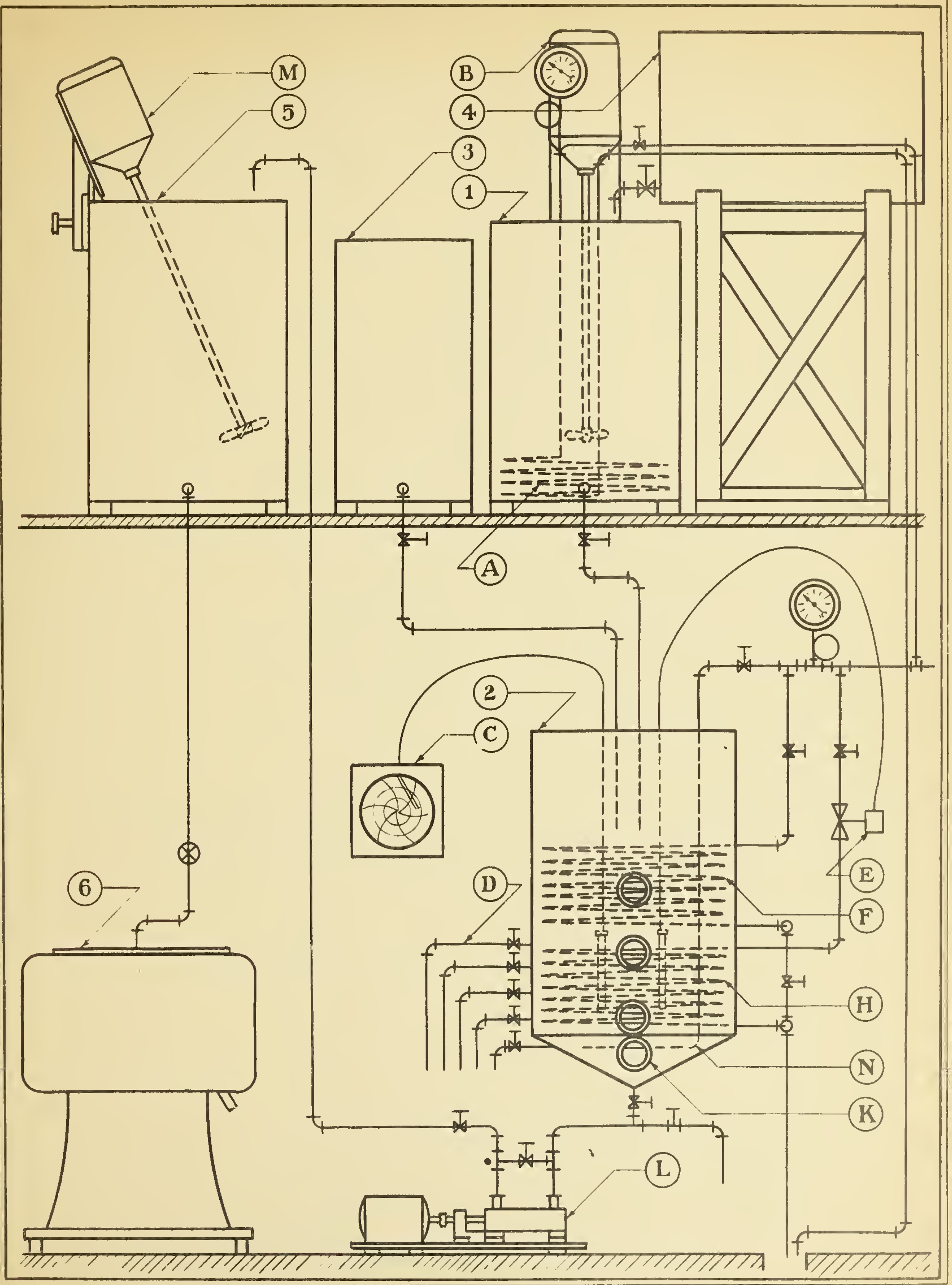

Fig I PILOT PLANT FOR ACONITATE RECOVERY
AGRICULTURAL CHEMICAL RESEARCH DIVISION, NEW ORLEANS, LA.

FIG. 2

FLOW SHEET FOR ACONITATE RECOVERY

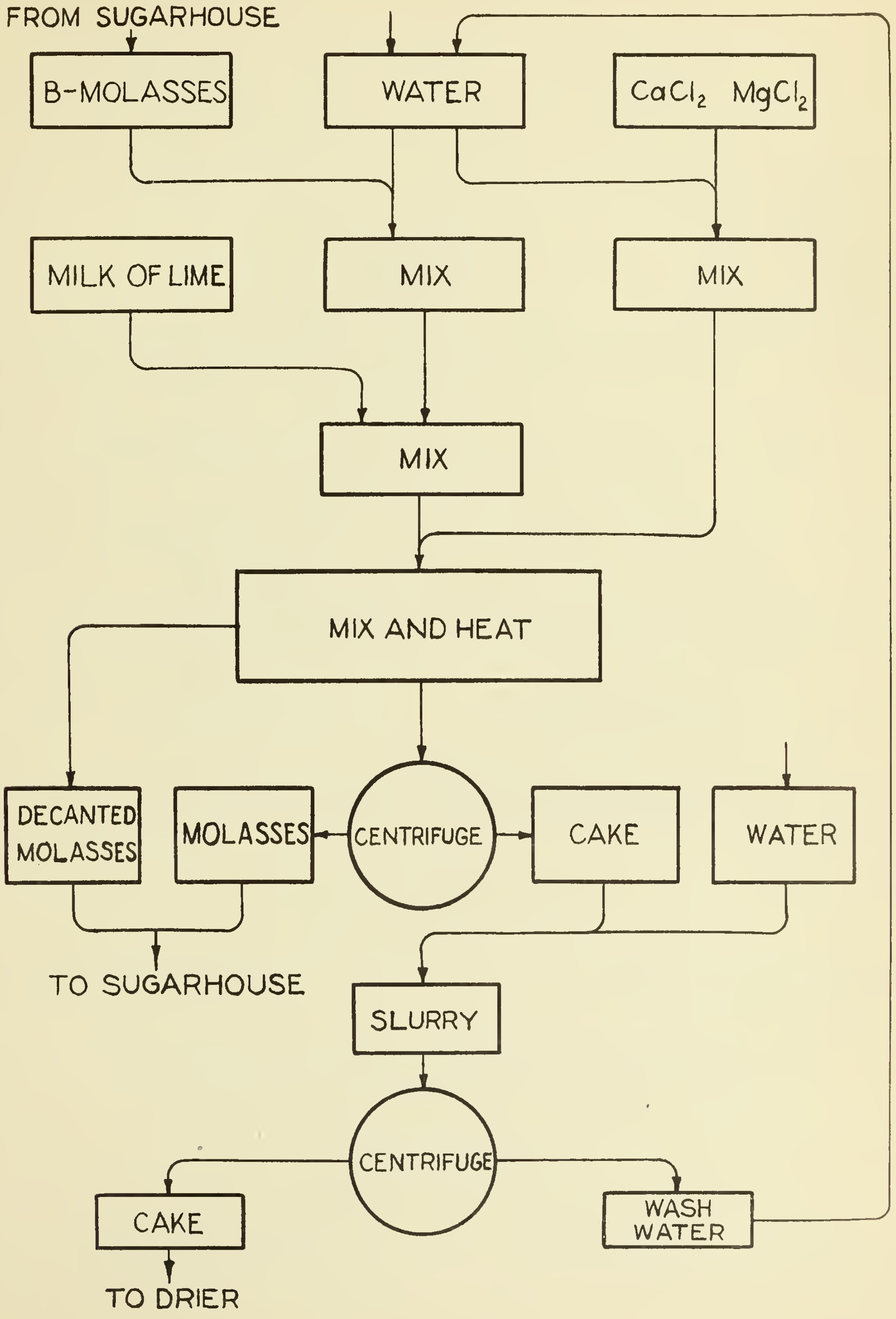

FIG 3

FLOW SHEET - PRODUCTION OF ITACONIC ACID